Trace elements in high pressure and temperature fluids in subduction zones

van Sijl, J.

2011

document version
Publisher's PDF, also known as Version of record

VRIJE UNIVERSITEIT

Trace elements in high pressure and temperature fluids in subduction zones

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan
de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. L.M. Bouter,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Aard- en Levenswetenschappen
op maandag 16 mei 2011 om 15.45 uur
in de aula van de universiteit,
De Boelelaan 1105

door

Jelle van Sijl

geboren te Deventer

promotor:	prof.dr. G.R. Davies
copromotoren:	prof.dr. N.L. Allan
	dr. W. van Westrenen

Reading committee:

dr. S. Jahn
GFZ German Research Centre for Geosciences, Potsdam, Germany

prof.dr. S. Klemme
University of Münster, Germany

dr. E. J. Meijer
University of Amsterdam, The Netherlands

prof.dr. C. Sanchez-Valle
ETH Eidgenössische Technische Hochschule, Zürich, Switserland

dr. P. Z. Vroon
VU University Amsterdam, The Netherlands

Nederlandse titel: *Sporenelementen in hoge druk en temperatuur vloeistoffen in subductie zones*

This work was financially supported by the Netherlands Organisation for Scientific Research, NWO/ALW grant number 816.01.002 and a EURYI award to dr. W. van Westrenen. Molecular dynamics simulations were performed on the HUYGENS and LISA high-performance computing clusters provided by the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF).

Total environmental impact of flights, experiments and computing (approximately):
26 tonnes CO_2 production, assuming a mixed sources energy supplier (0.55 kg CO_2 per kWh).
This has been compensated for by a private green energy investment.

Cover and book design: J. van Sijl
Typeset in Adobe InDesign CS4 with the Adobe Garamond® Pro and Ubuntu Font Families

Printed by Wöhrmann Print Service, Zutphen
ISBN: 978-90-8659-547-1

to

my teachers

Preface

With the completion of this dissertation, I've reached the summit of a long road of education; an accumulation of knowledge, skills and experiences that defines me and through which I interact with the surrounding world.
The work in front of you – that you have so courageously opened – is testimony to my journey to become an independent scientific researcher. It all started in Deventer, where my curiosity to discover Nature's inner workings came alive during my childhood and has since continued to intrigue me when listening to stories of plate tectonics, continental drift, mountain building, volcanism, climate, the formation of our solar system and the general state of affairs of humans and humanity in all these violent events. During my geology degree at Utrecht University, I discovered a wealth of specialist areas each tuned to unravel different aspects of planet Earth using the tools of physics, chemistry, biology and mathematics. Here, my fascination to use computers to conceptualise, model and quantitatively assess complex problems was born, and my work has more and more focussed on combining experimental with computational methods to investigate earth-scientific problems. If there is one thing however that can still sneak up on me by surprise it is the immensity of dimensionality – whether in space, time, temperature or pressure – that geologists are often dealing with so casually.

Of course I did not fly solo.
All those years, I've been educated, supported, trained and encouraged by a large number of people. I would like to take this opportunity to thank all these people, of whom I would like to mention some in connection to this dissertation:

I would like to thank my supervisor and mentor Wim for his continuing support and enthusiasm for my choices over the past four years. Wim, vanaf het begin van onze samenwerking stond je open voor mijn ideeën en keuzes. Doordat je deur altijd open was voor mij gaf je me de mogelijkheid om zelfstandig onderzoeker te worden, en gaf je me tegelijkertijd de steun en aanwezigheid die een promovendus vaak zo hard nodig heeft. Vooral de kritische blik waarmee je mijn geschreven werk bekeek en aanvulde met waardevol commentaar, en de inhoudelijke interesse in mijn modelleer-avontuur hebben de afgelopen vier jaar tot een succes gemaakt.

Neil, I could not have imagined a better mentor to support me in the sometimes quite convoluted world of (computational) chemistry. I enjoyed our countless chats on a range of subjects, our squash match (that you so cleverly won) and your delight in eating pancakes at the Pancake Factory. The amount of computational modelling in this dissertation directly relates to the positive experiences and continuing support from you during stays in Amsterdam and Bristol (please thank hotel Sue and your team in Bristol for being so kind to a Dutch geologist!). You were always interested in my geo-babble, never hesitating to point out the often quite different chemists' perspective. I hope that many PhD students in the future will benefit from your

indispensable input and support as I have.

At work, I've been surrounded by my colleagues and friends. I would like to thank them for keeping me busy and taking the pressure off with the inevitable after-work beers. In particular, I'd like to mention my office-mate Mirjam who with her motivation and driving force always continued to surprise me. Mir, your chats, choices and power have made my life at the VU much easier!
Elodie, the high-pressure lab would not have been the same without you. You are a meticulous, patient and careful experimentalist, who kept us going through difficult salt-cylinder pressing, piston-crushing, bomb-cracking and finger burning episodes. Your microprobe support has been indispensable to many, and I profited from this enormously at the critical point nearing completion.
Laura, I owe you a lot. Thanks for being such a good friend and colleague.
Raheleh, Daphne, Sander, Jane, Oliver, Jellie, Nachiketa, Esther, Josepha, Ibrahim, Jonathan and Suzy, thank you too!

Chris Spiers, Colin Peach, Pascal Winthaegen, Frank van Bergen, Bart Goes and Paul Meijer; I'm grateful for your guidance during my bachelors, masters and internship projects. Paul Mason and Helen de Waard, thank you so much for letting me work in the LA-ICPMS lab at Utrecht University, I'm pretty sure I could not have been able to set it up in Amsterdam without that experience. Fraukje Brouwer, thank you for believing in me at a difficult moment, and Pieter Vroon, thanks for providing opportunities in desperate times. Gareth Davies, thanks for bringing us up to speed with the latest 'political' issues and the general state of affairs on Thursday coffee meetings. Also, thank you for your last-minute speed-reading of my chapters, which – admittedly – are somewhat off-course relative to the common petrology curriculum.

The importance of highly skilled support staff is often underrated in a footnote or acknowledgements. Without the following people, my job would have been impossible. Op het gevaar af dat ik iemand vergeet, wil ik het werkplaats team bedanken voor hun inzet en hulp in het hoge druk ('Maan')-lab en mijn project. Dus Niek van Harlingen, Ron Lootens, Dick van Iperen, Roald Boegschoten, Rob van der Geer, Rob Limburg, Jaap Zwanenburg, Rob Stoevelaar, Hans Bakker, Wim van der Plas, Jan Veen, Fred Wolff, Vincent Kuipers, Jacob Arends, Rogier Elsinga en Daniel Pruyser: ontzettend bedankt!
John Visser en Bas van der Wagt, bedankt voor jullie hulp met chemicaliën en het rondsjouwen van de ICPMS!
Richard Smeets, Saskia Kars, Wynanda Koot, Bouk Laçet, Wim Lustenhouwer, Paul Smit, Roel van Elsas, Onno Postma en Fenny Bosse: Dank voor jullie hulp in het clean-lab, met de SEM, de EMP, in het mineraal-lab en alle administratieve zaken. Saskia, je fantastische SEM foto's en fijne werkplek (inclusief espresso) hebben me enorm geholpen!

I'd also like to thank the people from ETH Zürich for their hospitality, and in particular Alessandro Fabbrizio, Maarten Aerts and Peter Ulmer for their assistance in refining my diamond-trap skills and teaching me the tricks of the trade.

I'd like to thank my university friends Robert, Thomas, Geerke, Rolf and Leslie for many great adventures, and my old buddies Daniël and Anne for sticking with me for so many years, and the occasional guys-night out. Thanks also for Patrick de Zeeuw. I don't know how much our trip to Iceland contributed to choosing a career in petrology and structural geology, but it sure was fun!

To my parents Eliane and Wim and my two sisters Claartje and Gwen: ik kon mijn enthousiasme voor de aardwetenschappen altijd goed met jullie delen. Ik hou van jullie!

And last but not least, I'd like to thank Elodie for being more than colleague, room-mate and friend. Elo, your refined sense of humour, kindness, ideas and sharp debating skills kept me going through rough times and you mean more to me than I can express here.

Table of Contents

Introduction

Subduction zones

Physical and chemical processes taking place in subduction zones play a fundamental role in the geochemical cycle of many elements. Melting above subduction zones contributed to the formation of continental crust, setting the stage for the evolution of land-based organisms and causing the large-scale differentiation of the Earth's silicate mantle and crust. The development of chemical heterogeneities in the Earth's upper mantle is also controlled by subduction zone processes. The relevance of subduction zones to society today is that they are the locus of explosive volcanic eruptions, posing a direct (explosive ejecta, pyroclastic flows, tsunamis caused by volcano flank collapse) and indirect (e.g. agriculture and infrastructure destruction by volcanic ash) threat to a significant proportion of the world's population, for example in Indonesia and the Northern Mediterranean.

A large variety of volatile-rich material is fed into subduction zones, including marine sediments, altered oceanic crust and serpentinised mantle lithosphere (Hacker 2008). Hydration of oceanic crust occurs mainly at mid-ocean ridges. This is due to the high porosity and permeability of the mid-ocean ridge lavas in response to geothermal cycling, fissuring, normal faulting and volume decrease due to thermal contraction (Johnson and Pruis 2003; Ranero *et al.* 2003). Additional extensive slab hydration occurs due to bending of the oceanic plate during subduction via mechanisms of normal faulting that induce pressure gradients and downward fluid pumping (Faccenda *et al.* 2009), enhanced porosity due to pre-failure dilatancy and pre-existing cracks (Korenaga 2007) and migrating fluid filled cracks (Morgan and Holtzman 2005) that aid downward transport of fluids and storage of water in hydrous minerals in the oceanic plate and underlying mantle (Ohtani *et al.* 2004).

As a result, one of the most important chemical components in subduction zone processes is water. The descending subducting slab carries water-rich components to larger depths, where the increased temperatures and pressures cause fluids to be expelled. The release of water-rich fluids from the dehydrating slab into the overlying mantle wedge (Figure i-1) ultimately causes it to melt and generate magmas that feed into arc volcanic systems (Peacock 1990; Bebout 1995; Plank and Langmuir 1998; Schmidt and Poli 1998; Wallmann 2001; Jarrard 2003; Rüpke *et al.* 2004; Hacker 2008; Plank *et al.* 2009). In addition to water, arc magmas produced in subduction zone settings are enriched in other volatiles including CO_2, F, Cl, H_2S, and SO_2 compared to for example magmas erupting at mid-ocean ridges and ocean islands (Wallace 2005).

Constraining the chemical composition of liquids as they evolve from aqueous fluids to hydrous melts while ascending to the volcanic front is of critical importance: the concentration of elements in liquids at the pressure-temperature (P-T) conditions prevalent in the subducting slab determines to what extent elements are recycled into the deeper mantle. Likewise, chemical interaction between these liquids and the overlying mantle wedge determines to what extent the wedge composition can be modified (Poli and Schmidt 2002; Schmidt and Poli 2003). Ultimately, these liquids exert primary control on the origin of arc magmatism and its explosive surface expression, continental crust formation and the generation of economic ore deposits.

Under pressure and temperature conditions corresponding to the Earth's crust and uppermost mantle, the nature of these liquids changes from dilute aqueous solutions to solute-rich fluids or water-rich melts. Both, the solubility of H_2O in silicate melts and that of silicates

in aqueous fluids increases with increasing pressure and temperature until the miscibility gap between aqueous fluid and hydrous melt closes and the distinction between them vanishes (Kessel *et al.* 2005b; Manning *et al.* 2010). At present, progress in constraining the exact nature and role of subduction zone liquids is severely limited by insufficient knowledge on the nature of fluids and melts in equilibrium with mantle minerals at high P and T. Presently, most constraints are derived from a combination of measured trace element signatures in arc magmas, geodynamic models of subduction zones, experimental solubility -and element partitioning studies, *in situ* experiments and field observations of exhumed metamorphic and metasomatic rocks (Philippot and Selverstone 1991; Zack *et al.* 2002; Manning 2004; Antignano and Manning 2008; Manning *et al.* 2008; Plank *et al.* 2009).

Multiple interpretations of the geochemistry of arc magma

Slab-derived fluids are released almost continually down to depths of 150-200 km, during progressive dehydration of water-bearing minerals that reside in the colder parts of subducting slabs (Schmidt and Poli 1998; Hacker 2008). These fluids can act as carriers of chemical species from the subducting slab to the mantle wedge and through hydrous melting in the wedge, ultimately to parental island arc magmas. The trace element composition of island arc magmas differs substantially from that of non-arc magmas such as those erupting at mid-ocean ridges or ocean islands (see Figure i-2 and e.g. Tatsumi *et al.* 1995). Typical for magmas formed beneath arcs are their relative depletions in high field strength elements (HFSE: Nb, Ta, W, Ti, Zr and Hf) with concomitant relative enrichments in large ion lithophile elements (LILE: Sr, K, Rb, Ba and Pb) and light rare earth elements (REE, e.g. La, Ce), and elemental and isotopic compositions of B, Be, U and Th (Morris and Ryan 2004).

The exact origin of these signatures remains highly controversial. With respect to the decoupling of LILE and HFSE, one group of models suggests that during slab dehydration, light REE and LILE residing in the slab are preferentially enriched in fluids, while HFSE are retained in minerals in the solid slab residue that subducts further into the mantle (e.g. Brenan *et al.* 1995; Keppler 1996). A second group of models calls for selective HFSE retention into (accessory) minerals during fluid or melt interaction with the mantle wedge (e.g. Sorensen and Grossman 1989; Hermann 2002; Klimm *et al.* 2008; Hermann and Rubatto 2009). Be and Th-U systematics have been attributed to melting of the sediment layer on top of the subducting slab (Johnson and Plank 1999 and references therein) and to fluid release from the subducting oceanic crust (e.g. Kessel *et al.* 2005a and references therein), two models that require very different subduction zone temperature regimes.

Resolution of these controversies is essential for a better understanding of the dynamics and chemistry of subduction zones and has major implications for whole Earth chemical and geodynamic models. Answering these questions requires accurate knowledge of how elements distribute themselves between the relevant minerals and fluids as a function of pressure and temperature. Only when such distribution models become available can measured compositions of primitive arc magmas (Figure i-2) be inverted to reveal their origin.

A long-standing tenet of magmatic geochemistry is that the uptake of trace elements

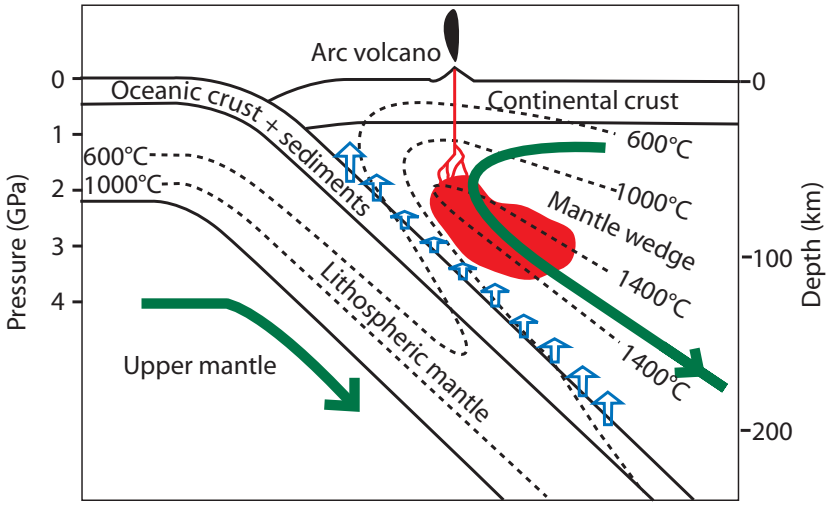

Figure i-1. Simplified sketch of a subduction zone (after Schmidt and Poli 1998), showing processes relevant to subduction zones: mantle flow (long arrows), fluid production by slab dehydration and subsequent ascent into the mantle wedge (open arrows), hydrous partial melting in the mantle wedge (red shaded field) and resulting arc volcanism. Selected isotherms are given as dotted lines.

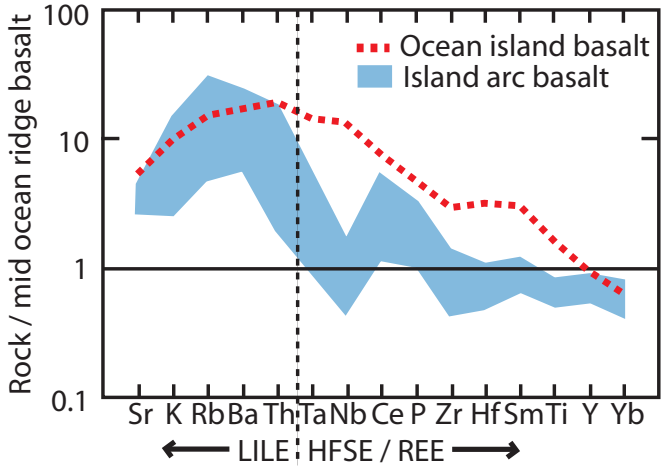

Figure i-2. Comparison of the average composition of island arc basalts and ocean island basalt with that of mid-ocean ridge basalt for selected trace elements (after Tatsumi and Eggins 1995).

into minerals is controlled by their equilibrium partition coefficient *D* (defined as the ratio of concentrations of an element in bulk mineral and co-existing melt). *D*-values between minerals and anhydrous melts are readily determined from high-temperature experiments. Unfortunately, our knowledge of mineral-fluid distribution for the elements shown in Figure i-2 is at present insufficient. Element partitioning varies with pressure, temperature, mineral and fluid chemistry and oxygen fugacity (e.g. Blundy and Wood 2003). The effect of each variable must be known for a large set of minerals to reliably predict element distributions in subduction zone settings.

The role of fluid chemistry in controlling mineral-fluid partitioning has not received a lot of attention, hindering the development of next-generation models. Despite abundant observations of fluid imprints in metamorphic and metasomatic rocks, the fluids have long since vanished and hence cannot be probed directly. On the other hand, high pressure and temperature experiments that aim to measure mineral-fluid partition coefficients *in situ* are scarce due to analytical challenges (e.g. Kessel *et al.* 2005a). It is well established that dissolved components may alter element partitioning (e.g. Antignano and Manning 2008), and that complexing anions such as fluoride and chloride may cause significant changes in trace element patterns, especially for the high field strength elements which are believed to be insoluble otherwise (Rubin *et al.* 1993; Van Baalen 1993; Keppler 1996; Rapp *et al.* 2010).

In this thesis, I use computer models of trace element complexation in subduction zone fluids and high-pressure, high-temperature mineral-fluid partitioning experiments to shed new light on the behaviour of key trace elements in subduction zone fluids.

Computer models of trace element complexation

Atomic-scale calculations of the energetics involved in mineral/melt trace element partitioning have proved to be a valuable tool for those modelling magmatic processes. Although this method does not explicitly yield absolute values for partition coefficients, it has been successfully applied to evaluate and rationalise experimental trace element data (e.g. Blundy and Wood 1994; Purton *et al.* 1996; Purton *et al.* 1997; van Westrenen *et al.* 2000; Allan *et al.* 2003; Blundy and Wood 2003; van Westrenen *et al.* 2003; van Kan Parker *et al.* 2010). Much computational work relies on classical molecular mechanics simulations that utilise parameterised interatomic force fields to describe the interactions in the system of interest.

The focus of these studies has been to unravel the energetics and atomic-scale mechanisms of mineral-melt trace element partitioning during for example mantle melting (Purton *et al.* 2000; van Westrenen *et al.* 2000; Brooker *et al.* 2003; Corgne *et al.* 2003; Du *et al.* 2008). These models assume the element distribution energetics are dominated by the more rigid mineral phases relative to the more compressible melts. At the same time, it has been noted experimentally that the local environment surrounding trace elements in melts can have a profound impact on partition coefficients (van Westrenen *et al.* 2001; Linnen and Keppler 2002; O'Neill and Eggins 2002; Blundy and Wood 2003; Schmidt *et al.* 2006).

Likewise, the effect of the local environment surrounding trace elements in aqueous fluids may be important, especially for fluids that exhibit elevated solute concentrations enriched in complexing ligands such as fluoride, chloride, carbonate, phosphate and sulphide

as are relevant to subduction zone settings. The solubility of minerals has become an important parameter to determine to what extent minerals are chemically resistant to fluid-fluxes derived from dehydrating slab -and mantle minerals (e.g. Klimm *et al.* 2008). The degree to which elements can be liberated by these fluids thus depends on lattice breakdown, but their relative mobility depends on (1) the stabilization of the solute species in solution, i.e. the complexation of ions by solvent molecules and (2) their incorporation into minerals that precipitate from or re-crystallise under the influence of the aqueous solution.

Our understanding of ion solvation in supercritical water, i.e. above the critical temperature and pressure of 647.096 K and 22.064 MPa (Wagner *et al.* 2000), is limited on account of experimental challenges. Classical mechanics can be used to describe mineral-water interaction (e.g. de Leeuw and Parker 1998). However, the development of accurate interatomic potentials to describe the interactions is challenging. Polarization effects at elevated PT-conditions are difficult to capture, transferability of the generated potential may be poor and the number of potentials required in the case of complexation with fluoride or chloride in aqueous solution is large (e.g. water-ion, water-water, water-F/Cl and ion-F/Cl). The problematic nature of interatomic potential development is nicely illustrated by the staggering number of studies devoted to developing accurate potentials for pure water alone (e.g. Vega *et al.* 2005; Kiss and Baranyai 2009).

To overcome these difficulties, I performed computer simulations of trace element solvation and complexation using a variety of electronic structure methods developed to approximately solve the Schrödinger equation for the electrons in a system, and evaluate the resulting total energies, forces and other quantities of interest. By making certain approximations to keep the problem computationally tractable, we look at aqueous complexation by chloride and fluoride of the Rare Earth Elements (REE, or lanthanides) and solvation at elevated pressures and temperatures applying density functional theory (DFT) to solvated clusters embedded in a continuum solvation model (Chapter 1).

Despite the improved insights in REE complexation energetics in solution, our understanding of the detailed structure and dynamics of hydration shells, as well as the effects of ions on the hydrogen bond network of liquid water under supercritical conditions remains incomplete. First-principles (*ab initio*) simulations are increasingly capable of providing valuable information that complement and extend experimental data. Car-Parrinello (CP) molecular dynamics (MD) methods (Car and Parrinello 1985) based on density functional theory (Hohenberg and Kohn 1964; Kohn and Sham 1965) (DFT) have proved particularly valuable. With these methods many-body interactions and polarization effects are taken into account and there is no reliance on empirically derived interatomic potentials which may be exploring the energy landscape beyond their regions of validity.

Taking Ti(IV) as representative to simulate the high-PT aqueous behaviour of the HFSE, we demonstrate the strength of *ab initio* molecular dynamics simulations to access details of element behaviour in aqueous fluids at geologically relevant conditions that are impossible to examine otherwise (Chapter 2). The results are further explored and rationalised in terms of dynamics of the ionic and electronic structure in Chapter 3, where we establish the fully atomistic and electronic nature of the hydrated Ti(IV) complex in solution under both ambient and supercritical conditions. In Chapter 4, we investigate the changes in local fluid structure and

solvation energetics upon aqueous complexation of Ti(IV) with fluoride or chloride at 1000 K and water densities relevant to subduction zone settings (from 0.6 – 1.5 g cm^{-3} approximately corresponding to a pressure of ~0.3 – 8 GPa). Simulations that make use of classical molecular mechanics methods are compared to fully *ab initio* DFT methods in Chapter 5, where we determine the energetics and mechanisms of tetravalent and pentavalent ion incorporation in TiO_2-rutile. By linking the mineral and fluid simulations, we establish a fully quantum mechanical picture of mineral-melt and mineral-aqueous fluid HFSE partitioning relevant in particular to subduction zone settings.

High pressure high temperature experiments

In line with the obtained atomistic insights of HFSE and REE solvation in supercritical aqueous fluids and their complexation with fluoride and chloride, we perform high pressure high temperature experiments at 900°C and 2.5 GPa on the common mantle mineral diopside ($CaMgSi_2O_6$) (Chapter 6). We conclude by combining evidence from high-PT experiments with simulation results to establish the role of complexing agents in aqueous solutions in determining trace element partitioning in subduction zone settings (Chapter 7).